Riverine particulate organic carbon from an active mountain belt: Importance of landslides

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[1] We investigate the routing and transfer of particulate organic carbon (POC) from the western Southern Alps, New Zealand, using organic carbon (C_{org}) and nitrogen (N_{org}) concentrations and stable carbon isotopes ($\delta^{13}C_{org}$). In this active mountain belt, sediment discharge is dominated by landslide-derived material. Landsliding acts to homogenize the geochemically diverse hillslope POC, mixing POC from the standing biomass and soil with the fossil POC from bedrock. As a result, the POC in river sediment at the mountain front is a binary mixture of fossil and nonfossil carbon sourced from many landslide deposits. We calculate that nonfossil biogenic POC makes up 63 ± 7% of the total POC in the suspended load of rivers draining the western Southern Alps. The erosional flux of biogenic POC from these catchments represents a transfer of 39 tC km^{-2} a^{-1} of atmospheric CO_2 averaged over the west flank of the mountain belt. If more than 10% of this POC is preserved in sediments on geological timescales, then this process is the most significant way in which the Southern Alps and similar, tectonically active mountain belts with restricted alluvial aprons consume atmospheric CO_2.

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1. Introduction

[2] The erosion of organic carbon from the continents and its transfer to the ocean constitutes an important component of the global carbon cycle. It is estimated that rivers deliver between 90 and 240 × 10^6 tC a^{-1} of particulate organic carbon (POC) to the ocean [*Ittekot*, 1988; *Berner*, 1992; *Meybeck*, 1993; *Stallard*, 1998; *Meybeck and Vörösmarty*, 1999; *Ludwig et al.*, 1996; *Chen et al.*, 2001]. This riverine POC transfer is comparable to the estimated global CO_2 consumption by silicate weathering of 104 × 10^6 tC a^{-1} [*Gaillardet et al.*, 1999].

[3] It has been suggested that fluvial transfer of POC is strongly correlated with the transfer of clastic sediment [*Ludwig et al.*, 1996]. A large proportion of the world's sediment discharge to the oceans originates in active mountain belts [*Milliman and Syvitski*, 1992]. High-standing, tectonically active islands in Oceania contribute ~33% of the total global clastic sediment input to the oceans from only ~3% of the Earth's landmass [*Milliman and Syvitski*, 1992] and the associated riverine POC transfer may constitute a similar proportion of the global riverine total [*Stallard*, 1998; *Lyons et al.*, 2002].

[4] Emergent, active mountain belts are likely to be important sources of POC delivered to the oceans. Firstly, they have small floodplains and therefore limited potential for subaerial storage and oxidation of sediment. Secondly, their clastic input to active margins drives very high sedimentation rates, for which the efficiency of organic carbon burial is high [*Canfield*, 1994]. Finally, many small mountain rivers discharge a significant amount of their total sediment load at hyperpycnal concentrations, where the density of the water sediment mixture at the river mouth is greater than that of the seawater into which it flows [*Mulder and Syvitski*, 1995; *Warrick and Milliman*, 2003; *Hicks et al.*, 2004a; *Dadson et al.*, 2005; *Milliman and Kao*, 2005]. Hyperpycnal plumes underflow seawater and may transfer sediment and POC direct into poorly oxygenated, deep marine basins. They may also cause rapid deposition of thick layers of sediment (decimeter to meter scale) in which organic carbon can be shielded effectively from oxidation.

[5] To assess the impact of riverine transfer of POC on the global carbon cycle, it is important to determine not only its magnitude but also the source of POC. Riverine POC is composed of fossil organic carbon, derived from sedimentary rocks, and nonfossil biogenic, organic carbon (either living biomass or recent, partially degraded material). The transfer of nonfossil biogenic POC to sedimentary basins will contribute to the drawdown of atmospheric CO_2 [*France-Lanord and Derry*, 1997]. In contrast, the transfer of fossil POC from sedimentary rocks to sedimentary basins has no impact on atmospheric composition at that time, while its oxidation will contribute CO_2 to the atmosphere.

[6] Published estimates of the fossil component of riverine POC in small mountain catchments range from less than 10% up to 75% [*Blair et al.*, 2003; *Komada et al.*, 2005; *Leithold et al.*, 2006]. These estimates are mostly for rivers affected by human activity [*Kao and Liu*, 1996; *Gomez et*

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al., 2004a], which may explain some of this variability. In order to assess the human impact on POC yields and the role of riverine POC transfer on longer timescales, it is important to understand the natural controls on carbon fluxes in unperturbed catchments. Moreover, many previously sampled catchments are located in accretionary tectonic settings [*Leithold et al.*, 2006] where weak sedimentary rocks build subdued relief. Little data is available on POC sourcing in mountain belts with high, steep topography in metamorphic bedrock [*Burbank et al.*, 1996; *Hovius et al.*, 1997]. In both settings river sediment yields are high but the mechanisms by which POC is harvested and routed from the catchments may not be the same [*Leithold et al.*, 2006], and the proportion of fossil and nonfossil POC in rivers and the likelihood of its sequestration may differ as a result.

[7] The west flank of the rapidly eroding Southern Alps, New Zealand, has minimal anthropogenic disturbance of natural vegetation. There, small mountain rivers export large amounts of sediment direct to the ocean [*Hicks and Shankar*, 2003]. The associated POC transfer has been estimated to be >20 times the global average [*Lyons et al.*, 2002; *Scott et al.*, 2006]. However, neither the source of the POC nor the mechanisms of its liberation and transfer have been identified, and the sustainability of the POC transfer remains to be established in the context of the net primary productivity (NPP) in the mountain belt. Here, we present new constraints on the source of riverine POC, using stable isotopes of organic carbon ($\delta^{13}C_{org}$) to distinguish between fossil and nonfossil sources. We then estimate the transfer of nonfossil biogenic POC and compare it with other significant carbon transfers from the west flank of the Southern Alps, and investigate the routing of the nonfossil materials on the mountain belt scale, using the bulk organic carbon to nitrogen ratio (C/N) of landslide deposits and suspended load [*Townsend-Small et al.*, 2005, *Holtvoeth et al.*, 2005].

2. Study Area

[8] The Southern Alps of New Zealand are a linear, asymmetric mountain belt formed along the oblique compressional boundary of the Australian and Pacific plates [*Walcott*, 1978]. Moisture-laden northwest winds from the Tasman Sea drive orographic precipitation of up to 10–15 m a^{-1} on the west flank of the mountain belt [*Griffiths and McSaveney*, 1983]. There, sustained rapid mass wasting and fluvial incision have exhumed high-grade metamorphic rocks at rates of up to ~7 mm a^{-1} [*Bull and Cooper*, 1986; *Tippett and Kamp*, 1993]. Along the range bounding Alpine fault exposed metasedimentary rocks of Mesozoic age [*Roser and Cooper*, 1990] have amphibolite grade mineral assemblages formed at 600–650°C and around 10 kbar. The metamorphic grade decreases eastward into the range to greenschist facies (450°C, 6–8 kbar) around the main divide [*Mortimer*, 2000]. Sediment discharge from the west flank of the mountain belt is dominated by landslide-derived material [*Hovius et al.*, 1997; *Korup et al.*, 2004], sourced on slopes with a modal steepness of 35°, and transferred in steep bedrock rivers without significant floodplains. The spatial and temporal patterns of landsliding over the last ~60 years are well known (Figure 1). Over this time interval landslides have occurred throughout the landscape, affecting high and low segments of hillslopes in equal measure, and sometimes clearing entire valley sides. The result is a patchwork of forest segments with different age and biomass.

[9] Below the tree line at ~1200 m, high rainfall supports temperate rainforest dominated by softwood/broad leaved hardwood C3 species: *Dacrydium cupressinum* (rimu), *Podocarpus dacrydiodes* (kahikatea), *Wienmannia racemosa* (kamahi), and *Metrosideros umbellata* (southern rata) [*Wardle*, 1984]. The aboveground standing biomass carbon store (including coarse woody debris) is large but variable, ~18,200 ± 12,600 tC km^{-2} (P. J. Bellingham, unpublished data, 2003). In long-lived hillslope hollows Acid Brown Soils, Orthic Podzols and Perch-Gley Podzols have developed and on alluvial patches Fluvial Raw Soils and Fluvial Recent Soils are found [*Tonkin and Basher*, 2001]. These soils tend to be organic carbon rich (5–27%) in the upper A_H horizons, but concentrations decline rapidly with increasing depth, approaching zero at ~15 cm depth [*Basher*, 1986]. Nevertheless, the montane soil carbon store is significant, ~6500–13,000 tC km^{-2} [*Coomes et al.*, 2003]. There is little anthropogenic disruption of the natural upland state in the western Southern Alps [*Leathwick et al.*, 2003] in stark contrast to other small mountainous rivers studied for POC yields [*Kao and Liu*, 1996; *Gomez et al.*, 2003].

3. Materials

3.1. River Sediment

[10] At or near the mountain front, samples of suspended sediment and bed material of 10 rivers were collected between 13 September and 6 October 2004 (Figure 2). Additional bed material samples were also collected along the course of the Copland River further into the mountain belt. Rivers were sampled while turbid and sampling was repeated up to three times during the field period. For each sample, 4 L of turbid water were collected from the surface of the main channel (in a vessel thoroughly rinsed with river water). At suspended load sampling sites, bed material was collected during low discharge. To do this, the upper ~2 cm of the river bed sediment were disturbed, and 4 L of sediment and water were collected in order to recover all fine-grained material.

[11] Samples were left to settle in order to separate particulates from the river water. The remaining fluid was filtered through 0.2 μm nylon membrane filters to catch the finest size fraction and this sediment was then added to the separated particulates. Filters were checked for damage after filtration to detect possible sample contamination. The sediment concentrate was then dried at <80°C to evaporate remaining water, and finally stored in airtight glass vials. Blanks (BK-1, $n = 3$) of quartz sand torched at 600°C for 3 h were subjected to the same filtration and drying procedure.

3.2. Landslide Debris and Bedrock

[12] Landslide deposits were sampled in August 2003. Fresh, unvegetated exposures of landslide debris were

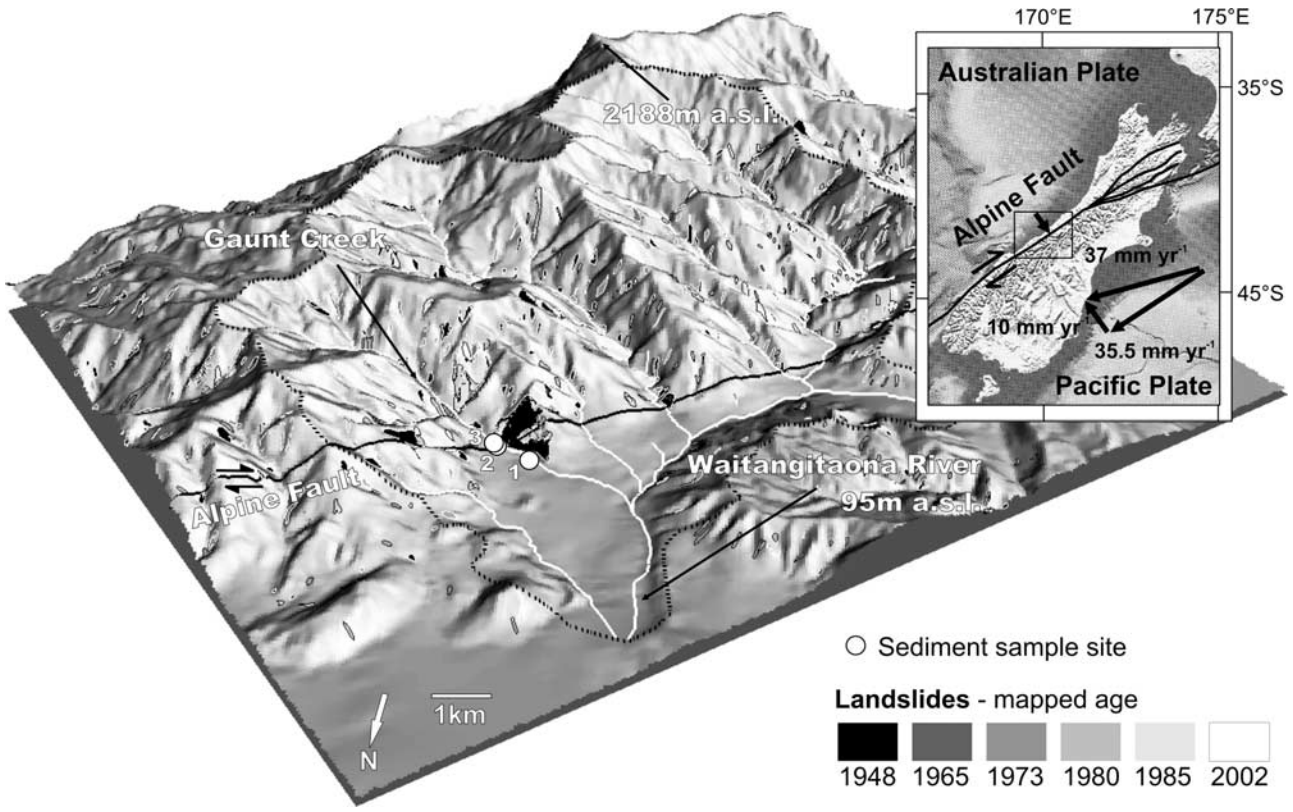

Figure 1. Waitangitaona River catchment in the western Southern Alps, New Zealand. Inset shows the regional tectonics of South Island, New Zealand. Box shows area of sampling (Figure 2), and arrow shows location of Waitangitaona catchment. Waitangitaona is a typical mountain river: Its upstream drainage area is ~70 km^2, and sediment yield ~12,500 t km^{-2} a^{-1} [*Korup et al.*, 2004]. Landslides are the dominant source of sediment [*Hovius et al.*, 1997]. Fresh landslide scars have been mapped from air photographs (1948, 1965, 1973, 1980, and 1985 [*Hovius et al.*, 1997]) and Landsat TM (2002, this study); shown are the temporal and spatial patterns of sediment production over the last ~60 years. Sediment samples collected for this study are also shown (also see Figure 2).

sampled at ~10 cm depth intervals from the top surface of the deposit. Samples consisting of approximately 125 cm^3 of material were dried at <80°C on the day of collection and then sieved to isolate the "sand" (63–500 μm) and "clay silt" (<63 μm) fractions. Together, these fractions span the size range of the riverine suspended sediment. Samples were collected from deposits of landslides with different size, area and prefailure vegetation maturity. These attributes were determined from time series air photographs, Landsat TM imagery and field observations in 1994, 2003, and 2004 (see Figure 1). All sampled sites are located close to the Alpine fault where exhumation rates are fastest.

[13] Sites 1, 2, and 3 are in Gaunt Creek, a tributary of the Waitangitaona River (Figures 1 and 2). Site 2 and 3 are in deposits of a large, slope-clearing landslide (area ~0.318 km^2, width ~300 m) which failed prior to 1948. This large but rare landslide is of a type that contributes significantly to the sediment export from the mountain belt [*Hovius et al.*, 1997]. The other sample sites are in smaller landslides that dominate the surface area disturbed by mass wasting due to their high frequency of occurrence [*Stark and Hovius*, 2001]. Site 1 was fed by small landslides (area ~0.010 km^2, width ~50–70 m) that scoured the large failure surface at Gaunt Creek. Site 4 is situated in the Whataroa catchment, in a shallow bedrock slide (area = 0.021 km^2, width ~35 m) with its crown at ~400 m asl, ~150 m below the ridge crest. This landslide reached the valley floor, spreading its debris on grassland ~800 m away from the river channel. Site 5, in the valley floor of Hare Mare Creek, was sourced by a small landslide (area = 0.010 km^2, width ~40 m) originating at the top of the adjacent hillslope, at an elevation of ~460 m asl.

[14] Site 1 was sourced after 1985 by landslides reactivating a surface that was previously cleared ~40 years earlier (Figure 1). Since then the hillslope has been chronically unstable [*Korup et al.*, 2004] and vegetation has not yet reached maturity. Similarly, at site 5 the source landslide occurred after 1985 on a surface previously cleared by a larger landslide prior to 1948. The large landslide connected to sites 2 and 3 occurred on a fully vegetated slope, and site 4 was supplied by a landslide that occurred after 1994 on a hillslope populated by dense, temperate rain forest.

[15] A suite of unweathered bedrocks were collected by *Pitcairn et al.* [2005] and as part of this study. Samples from

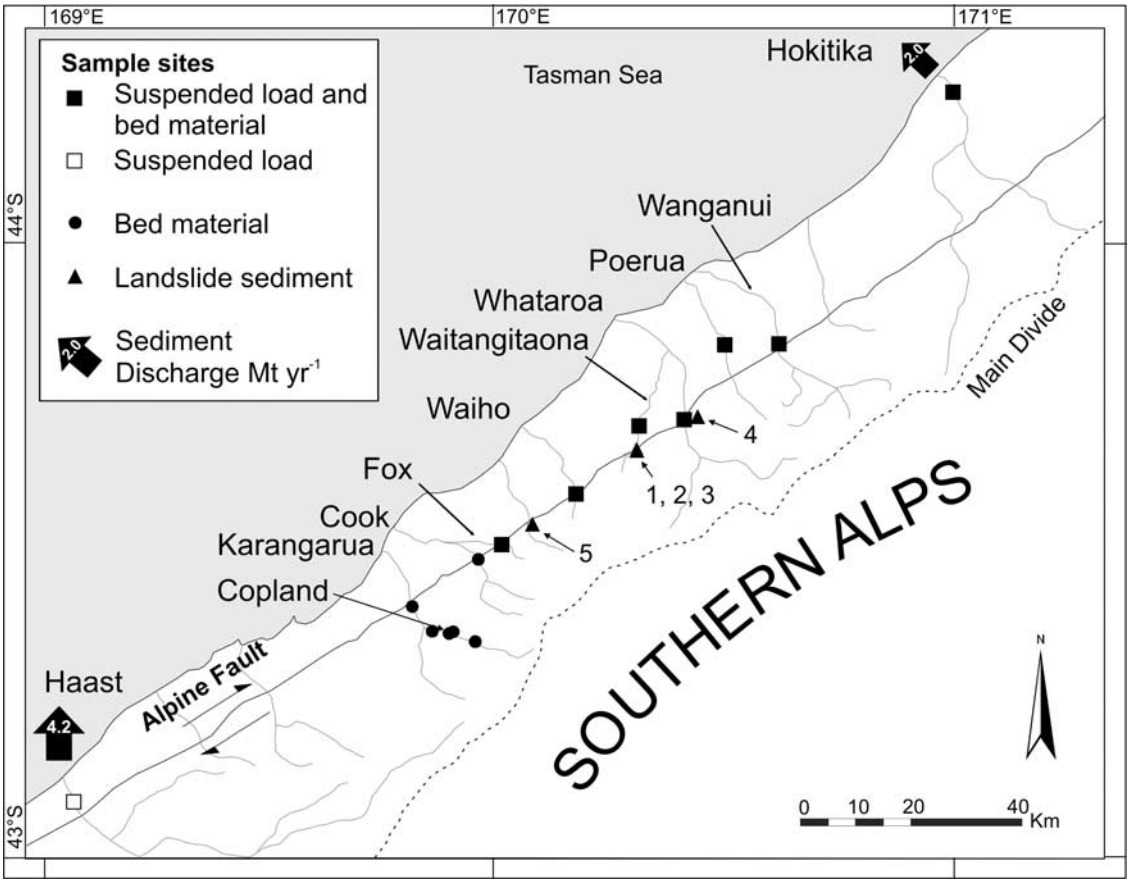

Figure 2. Suspended sediment, bed material, and landslide sediment sample locations. Arrows show published annual sediment discharge [*Hicks et al.*, 2004b].

the Alpine Schist were taken along cross-isograd transects in the Haast, Franz Josef and Fox catchments (Figure 2).

4. Methods

[16] All samples were homogenised by grinding in an agate mill. The ground mass was acidified with 6 N HCl and placed on a hotplate at <80°C for 4 h to remove carbonate [*France-Lanord and Derry*, 1994]. Blanks were subjected to the same procedure. Concentrations of organic carbon (C_{org}) and nitrogen (N_{org}) were determined by combustion at 1020°C in a Costech CHN elemental analyzer, using an acetanilide standard. All values reported for river sediment have been corrected for a full procedural blank average (BK-1) of C_{org} = 0.0033% N_{org} = 0.00032%. Landslide sediment and bedrock samples have not been filtered and have only been corrected for a blank average (BK-2, n = 3) of C_{org} = 0.0010% and N_{org} = 0.0018% corresponding to contamination from the homogenisation and carbonate removal steps.

[17] A subset of samples was analyzed for stable carbon isotopes on a Costech elemental analyzer coupled via a CONFLO III to a MAT 253 stable isotope ratio mass spectrometer. Reanalysis of samples after a year in storage has shown that the bulk C_{org} and N_{org} concentrations, and $\delta^{13}C_{org,}$ have not changed significantly after initial drying of the sample at 80°C in the field. Long-term reproducibility is to 2% and 4% for C_{org}, and N_{org}, respectively. The long-term reproducibility of $\delta^{13}C_{org}$ values is 0.06‰ based on 25 duplicate measurements of river suspended sediment.

5. Results

5.1. River Sediment

[18] Suspended sediment samples were collected at a range of suspended sediment concentrations (SSC) varying from 9.6 mg L^{-1} to 660 mg L^{-1} with a mean for all samples combined of 114 mg L^{-1} (Table 1). This is similar to the reported temporal mean SSC of the Hokitika and Haast rivers of 133 mg L^{-1} and 119 mg L^{-1}, respectively and comes close to the published flux-weighted average SSC of 645 mg L^{-1} and 700 mg L^{-1} for these two rivers [*Hicks et al.*, 2004b].

[19] The mean POC concentration in the river suspended load is C_{org} = 0.51 ± 0.12% which is at the lower end of values measured in other mountain rivers [*Kao and Liu*, 1996; *Masiello and Druffel*, 2001; *Gomez et al.*, 2003]. The mean POC concentration in river bed material is 0.23 ± 0.06% and for each catchment the ratio (bed material C_{org})/(suspended load C_{org}) is <1.

[20] The $\delta^{13}C_{org}$ of the river suspended load ranges from −22.70‰ to −28.02‰ with a mean of −24.9 ± 1.6‰

Table 1. Suspended Load (SL) and Bed Material (BM) Samples Collected During the Field Period[a]

River	Collection Date	Type	SSC, mg L^{-1}	C_{org}, %	C/N	$\delta^{13}C_{org}$, ‰
Hokitika	13/09/2004	SL	18.7	0.55	18.1	-
Hokitika	16/09/2004	SL	18.9	0.70	15.3	−26.04
Hokitika	23/09/2004	SL	9.6	1.00	12.9	−27.78
Hokitika	03/10/2004	BM	-	0.28	16.7	−26.02
Wanganui	16/09/2004	SL	86.2	0.44	14.7	−25.78
Wanganui	23/09/2004	SL	153.1	0.45	15.9	−26.79
Wanganui	03/10/2004	BM	-	0.15	12.1	-
Poerua	13/09/2004	SL	404.6	0.27	19.2	−23.04
Poerua	16/09/2004	SL	660.3	0.34	17.6	−23.45
Poerua	23/09/2004	SL	104.7	0.43	13.2	−24.58
Poerua	03/10/2004	BM	-	0.30	15.4	−24.05
Whataroa	16/09/2004	SL	40.7	0.89	22.5	−28.02
Whataroa	23/09/2004	SL	15.7	1.09	21.9	-
Whataroa	03/10/2004	BM	-	0.15	12.1	-
Waitangitaona	16/09/2004	SL	75.9	0.55	17.9	−24.64
Waitangitaona	23/09/2004	SL	38.4	0.77	20.1	−25.74
Waitangitaona	03/10/2004	BM	-	0.23	12.0	−22.70
Waiho	14/09/2004	SL	67.6	0.20	9.3	−24.12
Waiho	01/10/2004	SL	45.4	0.33	10.3	−24.22
Waiho	01/10/2004	BM	-	0.15	9.4	-
Fox	15/09/2004	SL	114.9	0.27	8.8	−23.77
Fox	18/09/2004	SL	122.7	0.31	12.1	−23.22
Fox	01/10/2004	BM	-	0.14	8.9	-
Cook	18/09/2004	BM	-	0.18	9.1	-
Cook	04/10/2004	BM	-	0.29	12.1	-
Karangarua	18/09/2004	BM	-	0.27	13.2	-
Karangarua	22/09/2004	BM	-	0.34	10.8	-
Karangarua	04/10/2004	BM	-	0.25	14.3	-
Copland – 1	22/09/2004	BM	-	0.38	11.8	-
Copland – 2	22/09/2004	BM	-	0.24	11.7	-
Copland – 3	22/09/2004	BM	-	0.20	12.5	-
Copland – 4	22/09/2004	BM	-	0.16	8.9	-
Haast	15/09/2004	SL	14.7	0.41	8.3	-
Haast	18/09/2004	SL	121.7	0.25	9.3	-
Haast	06/10/2004	SL	61.1	0.36	13.0	-

[a]Suspended sediment concentration SSC is displayed where measured (mg/L). C_{org} is organic carbon concentration (%), C/N is the bulk organic carbon to nitrogen ratio, and $\delta^{13}C_{org}$ the stable carbon isotopes of the organic carbon (‰).

(Table 1). When data from all sampled catchments along the western Southern Alps are combined, a correlation is found between C_{org} and $\delta^{13}C_{org}$ (Figure 3). When the isotopic composition and the concentration of the same chemical element are considered, the mixing of two distinct end-members defines a linear relationship between the inverse of the concentration (1/C) and the isotopic composition ($\delta^{13}C$). Thus the linear fit of the suspended load data (Figure 3) is most simply explained by a binary mixing of two end-members with distinct C_{org} and $\delta^{13}C_{org}$. Results for the three river bed sediments analyzed for $\delta^{13}C_{org}$ are consistent with the binary mixing as described by the suspended load (Figure 3).

[21] River suspended load has a mean C/N of 14.8 ± 2.1, with a range from 8.3 to 22.5 (Table 1). The mean C/N of bed material is 11.9 ± 1.7, with a range from 8.9 to 14.3, at the lower end of suspended load values.

5.2. Bedrock

[22] Measured bedrock samples have C_{org} ranging from 0.01% to 0.29% for the dominant quartz-feldspathic lithology (Table 2). The $\delta^{13}C_{org}$ ranges between −18.85‰ and −26.17‰ with a mean of $\delta^{13}C_{org} = -21.1 \pm 1.1$‰ (and an associated mean $C_{org} = 0.15 \pm 0.05$%). Thus bedrock has lower C_{org} and is isotopically heavier than the suspended sediment (Figure 3).

[23] Only five bedrock samples have N_{org} distinguishable from the blank. For these samples, C/N ranges from 4.8 to 18.9 with a mean of 9.0 ± 5.2 (with an associated mean $C_{org} = 0.17 \pm 0.10$%). This is within the range of values measured in sedimentary and metasedimentary rocks elsewhere [*Kao and Liu*, 2000; *Gomez et al.*, 2003].

5.3. Landslide Deposits

[24] In the five landslide sites, C_{org} ranges from 0.15% to 3.33% and there is marked variability between sites (Table 3). The mean C_{org} of the clay silt fraction ranges from 0.31 ± 0.01% at site 1 to 2.77 ± 0.51% at site 4. The mean C_{org} of the sand ranges from 0.15 ± 0.01% at site 1 to 2.31 ± 0.45% at site 4. There is marked homogeneity in C_{org} for each grain size fraction at each site (Table 3). The measured C/N ranges from 11.0 to 37.8. The mean C/N of clay silt ranges from 11.5 ± 0.5 at site 5 to 30.8 ± 4.7 at site 2. The mean C/N of sand ranges from 13.4 ± 0.8 at site 5 to 28.7 ± 7.4 at site 2.

[25] Depth transects reveal a lack of vertical trends in both C_{org} and C/N (Figure 4) at individual sites. There is no

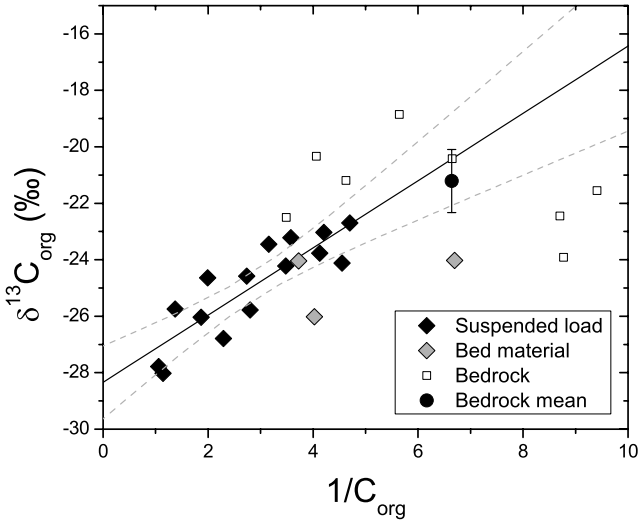

Figure 3. One over the organic carbon concentration ($1/C_{org}$) versus the stable carbon isotopes of the organic carbon ($\delta^{13}C_{org}$ ‰) of suspended sediment data (black diamonds), bed material (gray diamonds), and bedrock (white squares). Black line shows a linear fit through the suspended load data of $\delta^{13}C_{org} = 1.19 \pm 0.19 \times (1/C_{org}) - 28.34 \pm 0.60$ ($n = 15$; $R^2 = 0.86$; $P < 0.0001$). Dashed gray lines are 95% confidence bands. This linear trend implies a process or binary mixing control on the variables. Black circle shows the mean of the measured bedrocks ($n = 10$), and bars show standard error of the mean.

significant difference between the C/N for clay silt and sand fractions, although sand C/N is more variable than clay silt C/N (Figure 4). This means that the sampled landslide deposits are internally homogeneous on a scale of ~0.5 m at grain sizes <500 μm. At all sites, at all depths and for both grain size fractions, the C/N of the landside material is higher than the mean C/N of the bedrock samples.

6. Discussion

6.1. Riverine POC Transfer

[26] We have combined published estimates of suspended sediment transport for some rivers in the study area with our observations to estimate POC export (Table 4). Most of our suspended sediment sediment samples were collected at times when SSC was below the flux-weighted average SSC (Table 1) [*Hicks et al.*, 2004b], which may lead to an overestimation of POC transfer if an inverse relation between SSC and C_{org} is assumed [c.f. *Ludwig et al.*, 1996]. However, these small mountain rivers show a weak correlation between SSC and C_{org} and a nearly constant C_{org} at SSC above ~100 mg L^{-1} (Table 1). We therefore assume that the C_{org} values presented in this study are representative of average SSC conditions. We estimate that the mean POC yield from the western Southern Alps is 57 tC km^{-2} a^{-1} (Table 4). This is >30 times the global average [*Ludwig et al.*, 1996] and similar to estimates from other small mountainous catchments [*Gomez et al.*, 2003]. Our estimate of the specific yield of POC in the catchment of the Hokitika river, 47 tC km^{-2} a^{-1}, is similar to previous estimates of 43 and 44 tC km^{-2} a^{-1} [*Lyons et al.*, 2002; *Carey et al.*, 2005]. However, our estimate for the Haast catchment of 15 tC km^{-2} a^{-1} is much lower than the previous estimate of 71 tC km^{-2} a^{-1} [*Lyons et al.*, 2002], due in part to a downward adjustment of the sediment yield from the catchment from 12,700 t km^{-2} a^{-1} to 4500 t km^{-2} a^{-1} [*Lyons et al.*, 2005]. If the exhumation rate across the western Southern Alps is ~5 mm a^{-1} [*Bull and Cooper*, 1986; *Tippett and Kamp*, 1993], then the long-term sediment yields from this domain are ~12,500 t km^{-2} a^{-1}. Therefore the POC yield presented here for the Haast is a minimum. To prepare a further discussion of the riverine transfer of POC from the western Southern Alps we must first consider the origin of the POC.

[27] The $\delta^{13}C_{org}$ and C_{org} measured in suspended sediment define a binary mixing of two distinct end-members (Figure 3). One end-member is isotopically light and enriched in C_{org}, the other is isotopically heavy and depleted in C_{org}. The mean of carbon values measured in bedrock samples from the study area lies on the mixing line (Figure 3), and we propose that fossil POC in bedrock best defines the depleted end-member. The enriched end-member sits within the field of isotopic compositions characteristic of C3 vegetation growing at <2000m elevation [*Körner et al.*, 1988] and of soils in montane catchments [*Bird et al.*, 1994]. Therefore the range of concentrations and isotopic compositions of the POC in suspended sediment and bed materials of rivers in the western Southern Alps can be

Table 2. Bedrock Samples From the Alpine Schist[a]

Sample	Location	Lithology	Metamorphic Temperature, °C	Metamorphic Grade	C_{org}, %	C/N	$\delta^{13}C_{org}$, ‰
C50*	Franz Josef	QFS	550	garn	0.22	18.9	−21.19
C56*	Haast	QFS	600	garn-olig	0.15	-	−20.42
C61*	Haast	QFS	550	garn	0.18	-	−18.85
C66*	Haast	QFS	500	biot	0.29	4.7	−22.50
C70*	Haast	QFS	450	chlor	0.11	8.2	−22.45
C73*	Haast	MB	500	biot	0.01	-	−26.17
C75*	Franz Josef	QFS	600	garn-olig	0.08	-	−19.33
C76*	Haast	QFS	550	garn	0.11	-	−23.91
C77*	Haast	QFS	550	garn	0.11	-	−21.55
C84*	Haast	QFS	500	biot	0.25	8.5	−20.33
BR 1	Fox	QFS	-	-	0.01	4.8	-

[a]Asterisk indicates samples collected by I. K. Pitcairn [*Pitcairn et al.*, 2005]. Metamorphic grade and temperature are from *Pitcairn et al.* [2005]. QFS are samples of quartzo-feldspathic schist, and MB is a metabasalt. C_{org} is organic carbon concentration (%), C/N is the bulk organic carbon to nitrogen ratio, and $\delta^{13}C_{org}$ the stable carbon isotopes of the organic carbon (‰). No value indicates N_{org} was indistinguishable from the blank.

Table 3. Landslide Sediment Data[a]

Site	Depth, m	Clay Silt (C_{org}, %)	C/N	Sand (C_{org}, %)	C/N
1	0	0.33	19.2	0.16	28.1
1	0.12	0.32	18.7	0.15	11.8
1	0.24	0.30	25.0	0.15	20.9
1	0.36	0.30	18.9	0.15	20.5
1	0.48	0.32	20.1	0.16	14.5
1	0.6	0.30	21.2	0.15	15.8
Mean		0.31 ± 0.01	20.5 ± 2.4	0.15 ± 0.01	18.6 ± 5.8
2	0	0.56	28.2	0.30	22.6
2	0.15	0.57	34.2	0.32	31.6
2	0.3	0.45	28.6	-	-
2	0.45	0.54	37.2	0.26	22.8
2	0.6	0.54	25.8	0.26	37.8
Mean		0.53 ± 0.05	30.8 ± 4.7	0.28 ± 0.03	28.7 ± 7.4
3	0	0.44	21.1	0.28	25.4
3	0.3	0.56	30.5	0.25	16.3
3	0.6	0.54	30.8	0.20	19.4
3	0.9	0.61	23.9	0.27	30.7
3	1.2	0.56	33.8	0.25	21.2
3	1.5	0.47	27.1	0.29	33.7
3	1.8	0.54	31.6	0.30	32.5
3	2.1	0.47	32.8	0.27	26.1
Mean		0.52 ± 0.06	28.9 ± 4.5	0.26 ± 0.03	25.7 ± 6.4
4	0	2.82	23.0	1.89	34.7
4	0.3	2.72	26.3	2.74	36.6
4	0.6	3.01	26.3	2.43	23.0
4	0.9	1.82	27.5	1.68	23.9
4	1.2	3.33	23.3	2.80	23.8
4	1.5	2.92	25.4	2.30	22.0
Mean		2.77 ± 0.51	25.3 ± 1.8	2.31 ± 0.45	27.3 ± 6.5
5	0.15	0.75	11.6	0.49	14.7
5	0.3	0.71	11.5	0.49	13.2
5	0.45	0.63	11.0	0.34	12.8
5	0.6	0.63	12.4	0.31	13.6
5	0.65	0.74	11.2	0.31	12.2
5	0.8	0.68	11.2	0.30	13.6
5	1	0.78	11.3	0.38	13.8
Mean		0.70 ± 0.06	11.5 ± 0.5	0.38 ± 0.08	13.4 ± 0.8

[a]Organic carbon concentration (C_{org}) and organic carbon to nitrogen ratio (C/N) are shown at different depths at each site for the clay silt (<63 μm) and sand (63–500 μm) grain sizes. Mean for each site shown with standard deviations.

explained by variable contributions of organic carbon from a biomass and soil source added to organic carbon contained as fossil POC in mobilized bedrock.

[28] The measured concentration and isotopic composition of POC in sediment can be used to determine the relative contributions from these sources. This can be done in two ways. One considers only the C_{org} of the sediment and assumes that any enrichment of organic carbon in the suspended load, above the C_{org} of the fossil end-member, is due to an addition of nonfossil POC. For this purpose, the fossil POC end-member is assigned the mean measured bedrock value of C_{org} = 0.15%. The other method makes use of the isotopic composition of the carbon. The fossil POC, end-member is assigned a value of $\delta^{13}C_{org}$ = −21.1‰, the mean value measured in bedrock, and the nonfossil end-member is attributed a value of $\delta^{13}C_{org}$ = −28.3‰, obtained by extrapolation of the best fit to the data (Figure 3). These two approaches produce compatible estimates of the fraction of fossil POC, with an average discrepancy of 0.03. There are more measurements of C_{org} than of $\delta^{13}C_{org}$ (Table 1), and on the basis of this characteristic we estimate that the fossil fraction of POC in river suspended load is on average 0.37 ± 0.07, with a range of 0.13 to 0.75 (Table 4), comparable to estimates from other small mountain rivers [*Kao and Liu*, 1996; *Masiello and Druffel*, 2001; *Blair et al.*, 2003; *Komada et al.*, 2005; *Leithold et al.*, 2006]. Thus the fossil contribution to the POC load is large despite the dense hillslope organic carbon store, minimal upland anthropogenic disturbance and low C_{org} in metasedimentary bedrock in the western Southern Alps.

[29] Using the mean suspended load C_{org} and the mean fraction of nonfossil C_{org} for each catchment (Tables 1 and 4), the mean nonfossil biogenic POC transfer for the western Southern Alps is 39 tC km^{-2} a^{-1}, ranging from 9 to 87 tC km^{-2} a^{-1} for individual catchments (Table 4). These POC yields do not account for bedload transport which can represent as much as 50% of the total riverine transport of sediment in an active orogen [*Galy and France-Lanord*, 2001; *Dadson et al.*, 2003], and may contain a significant amount of biogenic POC when coarse woody debris is rigorously considered. The suspended sediment transfer of nonfossil POC represents ∼0.1% of the hillslope carbon store of ∼28,000 tC km^{-2} [*Coomes et al.*, 2003] and ∼4% of the annual net primary productivity of ∼1100 tC km^{-2} a^{-1} [*Whitehead et al.*, 2002]. From this we conclude that the high measured yields of nonfossil POC are sustainable on long timescales in a densely vegetated biome undergoing rapid uplift and erosion, such as the western Southern Alps.

[30] *Burdige* [2005] has estimated the burial efficiency of terrestrial organic matter (relative to the riverine input) for nondeltaic continental margin sediments at ∼17%, and at sediment accumulation rates greater than 0.1 g cm^{-2} a^{-1} measured burial efficiency is consistently above 10%. *Galy et al.* [2007] have reported even higher burial rates in the Bay of Bengal. On margins receiving sediment from small mountain rivers, sedimentation rates may approach 5 g cm^{-2} a^{-1} [*Gomez et al.*, 2004b]. Moreover, rivers draining the western Southern Alps may on occasion discharge large amounts of sediment to the ocean at hyperpycnal concentrations [*Mulder and Syvitski*, 1995]. Hyperpycnal river plumes can turn into turbidity currents and result in thick sediment beds. Thus they provide a mechanism for delivering terrestrial POC rapidly to deep sea depocentres [*Walsh and Nittrouer*, 2003; *Nakajima*, 2006] and for shielding deposited POC from oxygenated ocean water. Therefore it seems reasonable to assume that at least 10% of the POC output from the western Southern Alps is preserved in long-lived sedimentary deposits. At this conservative preservation rate, the transfer of eroded biogenic POC to sediment is ∼4 tC km^{-2} a^{-1}. Considering that the rate CO_2 drawdown by silicate weathering in the same area is 3.5 tC km^{-2} a^{-1} [*Jacobson and Blum*, 2003; *Lyons et al.*, 2005], the transfer and burial of nonfossil biogenic POC is likely to be the more significant way in which the Southern Alps consume atmospheric CO_2 on geological timescales. By extrapolation, the harvesting and burial of modern biogenic POC in basins fed by steep river catchments in active mountain

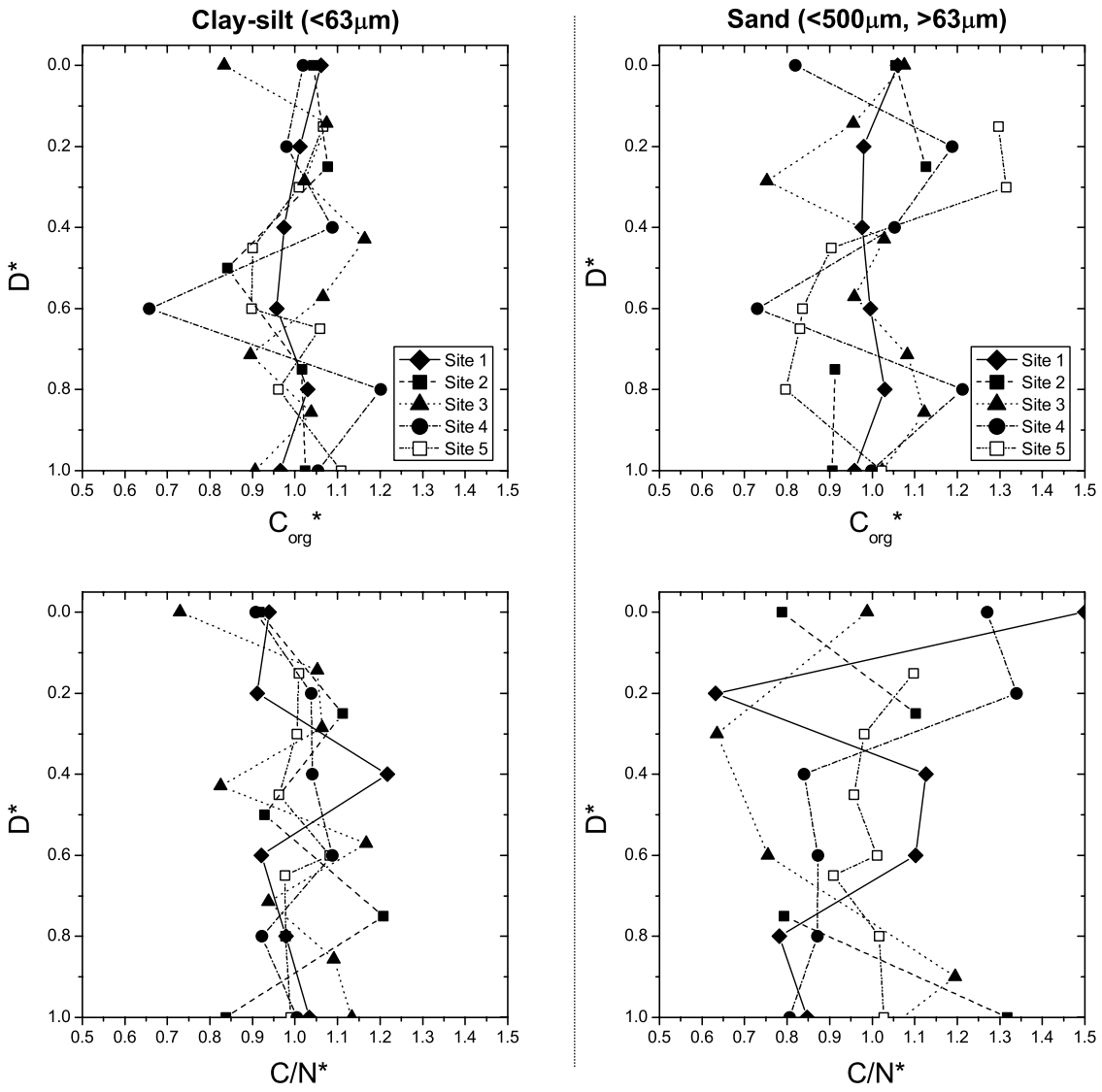

Figure 4. Depth transects for each site for clay silt (<63 μm) and sand (<500 μm, >63 μm) size fractions. D* is normalized depth; normalized to deepest point on the transect (Table 3). C_{org}* and C/N* are organic carbon concentration and organic carbon to nitrogen ratio normalized to the site means (Table 3). There are no discernable vertical trends in all deposits in both size fractions.

belts could be a globally significant mechanism of atmospheric CO_2 drawdown on long timescales.

6.2. Routing of POC

[31] The occurrence of a single nonfossil end-member is intriguing, given that at the scale of individual plant species, litters and soils there can be a large range in both $\delta^{13}C_{org}$ [*Guehl et al.*, 1998] and C_{org} [*Hart et al.*, 2003]. The $\delta^{13}C_{org}$ of soils and vegetation tend to overlap in montane catchments [*Bird et al.*, 1994; *Townsend-Small et al.*, 2005]. The variable proportion of nonfossil POC in the riverine sediment (Table 4) could therefore represent a fairly stable amount of POC derived from rock and soil but a variable contribution from vegetation. The C/N of POC can be used to distinguish between nonfossil carbon from soil and vegetation [*Townsend-Small et al.*, 2005; *Holtvoeth et al.*, 2005]. C/N is 16 to 25 in surface soil horizons [*Basher*, 1986]. By contrast, in C3 vegetation in an indigenous montane forest ecosystem similar to that studied here, C/N is around 40 in the leaf component, 78 to 157 for twigs and small branches, through ~250 for bark, to >600 in stem wood [*Hart et al.*, 2003].

[32] Unlike the C_{org} and $\delta^{13}C_{org}$ data, the C/N and C_{org} data for river sediment in the western Southern Alps shows significant scatter. Hence a simple binary mixing model described by the linear best fit with $C/N = (a \times C_{org} + b)/(c \times C_{org} + d)$ does not describe the data well, $R^2 = 0.29$ (Figure 5a). Some of the suspended sediment and most of the bed material have C/N and C_{org} close to the average composition of the Alpine Schist bedrock (Figure 5a), reemphasising the significant contribution of fossil POC from bedrock inferred from $\delta^{13}C_{org}$. Therefore scatter in the

Table 4. Mean Measured Organic Carbon Concentration (C_{org})[a]

River	Mean C_{org}, %	Annual Sediment Yield, t km^{-2} a^{-1}	POC Yield, tC km^{-2} a^{-1}	Fraction Nonfossil POC	Nonfossil POC Yield, tC km^{-2} a^{-1}	Silicate Weathering CO_2 Consumption, tC km^{-2} a^{-1}	Drainage Area, km^2
Hokitika (n = 3)	0.75	6313[b]	47	0.80	38	3.6[b]	352
Wanganui (n = 2)	0.45	12,500[c]	56	0.66	37	1.7[d]	344
Poerua (n = 3)	0.35	26,200[e]	91	0.57	52	1.7[d]	136
Whataroa (n = 2)	0.99	10,325[b]	102	0.85	87	10.1[b]	453
Waitangitaona (n = 2)	0.66	12,500[f]	83	0.77	64	1.7[d]	72
Waiho (n = 2)	0.26	10,325[b]	27	0.43	12	1.7[d]	164
Fox (n = 2)	0.29	12,500[c]	37	0.49	18	1.7[d]	92
Haast (n = 3)	0.34	4500[b]	15	0.56	9	6.0[b]	1020

[a]Number of observations for each river is given by n. Mean values of C_{org} are combined with published estimates of annual sediment yield to estimate POC yields. Nonfossil POC yields are calculated using mean fraction of nonfossil POC (see text) combined with POC yields.
[b]Data from *Lyons et al.* [2005].
[c]No data: Sediment yield estimated assuming uniform exhumation of 5 mm a^{-1} over the catchment and a uniform rock density of 2500 kg m^{-3}.
[d]Data from *Jacobson and Blum* [2003].
[e]Data from *Korup et al.* [2004], over period 05/99–02/02 assuming average rock density 2500 kg m^{-3}.
[f]Data from *Korup et al.* [2004].

C and N composition of the suspended material is more likely to reflect a highly variable contribution of soil and vegetation. For example, the Hokitika River is characterized by the mixing of bedrock and soil material, the Poerua River has nonfossil POC derived mainly from vegetation, and nonfossil POC in the Whataroa and Waitangitanoa Rivers appears to be a mixture of materials derived from soils and vegetation (Figure 5a and Table 1). Notwithstanding this complexity, our data suggest that at the catchment scale, mobilization of POC occurs by processes that reduce the heterogeneity of the nonfossil POC and mix it with significant amounts of fossil POC from bedrock.

[33] The processes by which this mixing occurs can be examined by looking at landslide deposits and the nature of POC within individual deposits. Hillslopes in the western Southern Alps have significant stores of carbon in standing biomass, partially degraded litter and coarse woody debris, and surface soils [*Coomes et al.*, 2003; P. J. Bellingham, unpublished data, 2003]. The measured compositions of POC in landslide debris occupy a section of the ternary mixing space of bedrock, soil and vegetation end-members larger than the river sediment discussed above (Figure 5b) However, their range is restricted when compared with C_{org} and C/N measured in soil and vegetation, and values for POC in landslide debris plot very near the bedrock end-member. This shows that POC from vegetation, soil and bedrock have been mixed in landslide debris.

[34] All sampled landslide deposits show a lack of vertical trends in profiles of both C_{org} and C/N (Figure 4). This homogeneity most likely originates from destruction, and effective mixing of hillslope biomass and soil with bedrock during mass wasting. In addition, the ratio of C_{org} in the clay silt/sand fractions is always >1 (Table 3). This may not be expected for landslide sediment where fresh bedrock may have been broken into a large range of grain sizes. It suggests that POC is dominantly fine grained and that a large proportion of the POC is probably associated or bound to mineral surfaces. As mean C/N values are very similar for the clay silt and sand fractions in landslide debris (Table 3), the POC at these grain sizes has essentially identical sources. Its concentration is set by mineral dilution. Taken together, these observations suggest that the composition, concentration and distribution of POC in landslide debris are due to a combination of two processes. Landsliding harvests bedrock, soil and standing biomass. During downslope transport the grain size of this material is mechanically reduced, and contributions from different sources are mixed. This results in homogenization of POC in landslide debris, and a dilution of high concentrations of POC in soil and

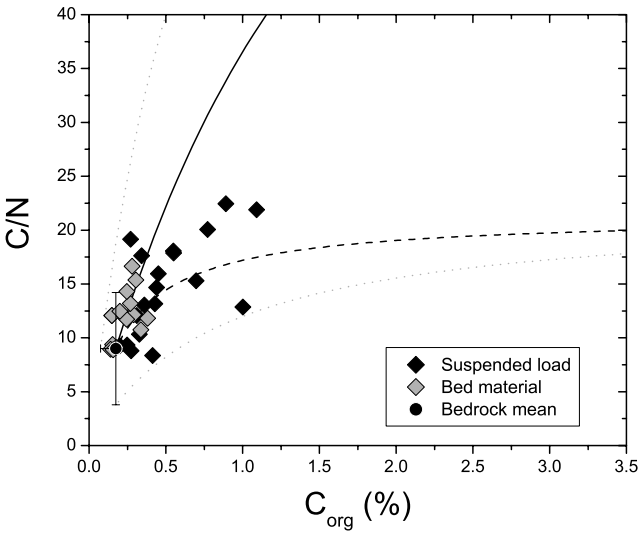

Figure 5a. Organic carbon concentration (C_{org}) versus organic carbon to nitrogen ratio (C/N) for suspended load (black diamonds) and bed material (gray diamonds). Black circle corresponds to the mean of the measured bedrock (Table 2). Solid and dashed curves represent the mixing of POC from bedrock with POC from vegetation and soil, respectively. Dotted lines represent the extent of the mixing envelope considering the range of measured values of bedrock, soil, and vegetation (Table 2) [*Basher*, 1986; *Hart et al.*, 2003]. Suspended load data lie within the range of values expected from a mixture of vegetation, soil, and bedrock.

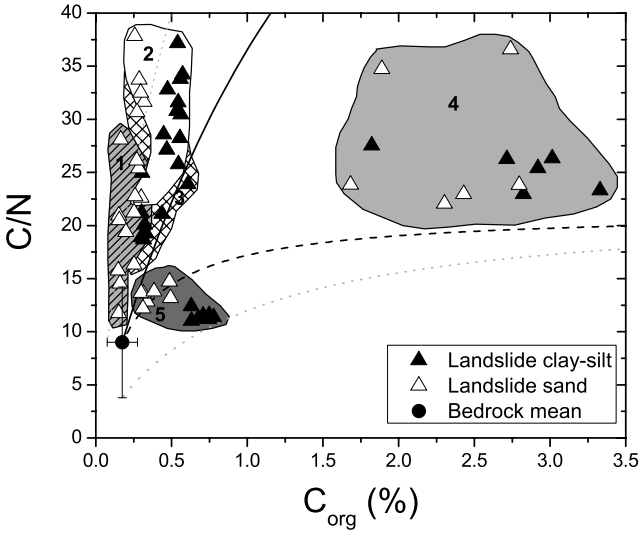

Figure 5b. Landslide sediment samples together with the same mixing relationships (Figure 5a). Solid and open triangles show clay silt (<63 μm) and sand (<500 μm, >63 μm) fractions, respectively. Numbers correspond to each landslide site (Table 3).

vegetation materials through addition of fragmented bedrock material with much lower POC concentrations. However, this mechanism cannot fully explain the dominance of fine POC in landslide deposits and its association to mineral surfaces. These attributes are likely to be due to pedogenic processes [*Sollins et al.*, 1996] acting on hillslope materials prior to slope failure, and on landslide debris after deposition.

[35] Given that the POC in landslide debris is a mixture of materials from fossil and nonfossil sources, the bedrock end-member (Figure 3) can be used to estimate that the nonfossil component of the POC ranges from 0% to 95% of the total. Considerable intersite variability, seen both in C_{org} and in C/N (Figure 5b), can best be explained with reference to the characteristics of the sampled landslides. The depth of a landslide sets the relative bedrock contribution, and the state of hillslope vegetation prior to landsliding determines the biogenic input to landslide debris. In agreement with this notion, in the small, shallow landslide of site 4 the mean C_{org} is 4 to 6 times higher than at sites 2 and 3 in debris sourced from a large, deep failure with a greater contribution from the bedrock. Moreover, the differences in C_{org} and C/N between these sites (Figure 5b) may reflect differences in the source of the nonfossil carbon–standing biomass for sites 2 and 3, and soil and biomass for site 4. Site 5 was fed by a recent landslide located within an older (>60 years), larger landslide scar on which vegetation had not reached full maturity when failure reoccurred. In contrast, site 4 was sourced from a slide that disrupted mature forest. Lower values of C_{org} and C/N at site 5 relative to site 4 (Figure 5b) may reflect depleted biomass and thin soil in the source area of site 5 prior to failure. Together, the five sites at which we have sampled landslide deposits span a range of source areas from $\sim$0.01 km^2 to $\sim$0.3 km^2. This covers a substantial segment of the total size range of landslides mapped in the western Southern Alps [*Hovius et al.*, 1997]. Therefore we are confident that our sample of landslide deposits should provide a reasonable constraint on the composition and abundance of POC contained in landslide debris throughout the mountain belt.

[36] At the mountain belt scale a large number of bedrock landslides contribute sediment to rivers [*Hovius et al.*, 1997]. For example, analysis of a time series of aerial photographs has revealed that in the Whataroa catchment alone (Figure 2) at least 315 landslides occurred between 1965 and 1985. If rivers source their sediment and POC mainly from the numerous landslide deposits in their catchment area, then the POC load of a river at the mountain front represents the integral of contributions from all active landslide sources. Mixing of the biogenic POC from different hillslope stores has already happened in the landslides (Figure 5b), and this is why the composition of POC in river suspended load can simply be described as a binary mix of material from fossil and nonfossil sources (Figures 3 and 5a). Surface runoff, which can deliver organic rich particulate material from standing biomass and litter, cannot explain the large fossil POC component measured in the rivers of the western Southern Alps. Landslides explain the low biogenic component in the riverine POC (of 63 ± 7%) and should be important in the routing of POC from other rapidly uplifting mountain belts where metamorphic bedrock builds steep topography.

7. Conclusions

[37] Using the organic carbon concentration (C_{org}), stable carbon isotopes ($\delta^{13}C_{org}$) and the organic carbon to nitrogen ratio (C/N) we have determined the main sources of POC exported by rivers from the tectonically active western Southern Alps, New Zealand, where anthropogenic disturbance is minimal. There, landslides mobilize standing biomass and soil POC and dilute it with bedrock. Their deposits comprise a mixture of these sources. At grain sizes <500 μm they contain between 0% and 95% nonfossil biogenic POC. Variations between landslide deposits are a consequence of differing vegetation state of the hillslope prior to failure, and the depth of the landslide (i.e., proportion of bedrock). Mechanical breakdown of coarse POC and mixing during mass wasting and pedogenic processes that associate organic carbon with mineral grains act to homogenize POC within deposits. At the catchment scale, rivers source POC from many landslide deposits and heterogeneities are integrated. As a consequence the suspended load can be described by a binary mixing of fossil and nonfossil POC. We estimate that 63 ± 7% of the suspended load POC is from nonfossil biogenic sources. This is similar to estimates from mountain rivers elsewhere despite the dense hillslope organic carbon store ($\sim$28,000 tC km^{-2}), C_{org}-poor metasedimentary bedrock, and minimal upland anthropogenic disturbance in the western Southern Alps, and we attribute dilution of nonfossil POC to the dominant role of bedrock landsliding in the mobilization of POC in this mountain belt.

[38] In the western Southern Alps the atmospheric CO_2 transfer via transport of terrestrial biogenic POC is on average 39 tC km^{-2} a^{-1}, an order of magnitude greater

than the published CO_2 consumption by silicate weathering in the same area. The huge hillslope carbon store and high net primary productivity mean that the POC transfer is sustainable on long timescales. If 10% or more of this POC escapes oxidation, which is likely on active margins where continental sediment supply is high, then the harvesting of POC from hillslopes and its sequestration in foreland sediments is the most significant way in which this active mountain belt impacts atmospheric composition. This may be true for many active orogens drained to the ocean by short, steep rivers, which are known to account for a large proportion of the global riverine POC transfer.

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